Introduction to Polymer Science
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Lecture - 32
Mass Spectroscopy of Polymers

Welcome back. In this lecture, I will complete the module on polymer characterization and I will discuss about mass spectroscopy of polymers and chemical characterization.

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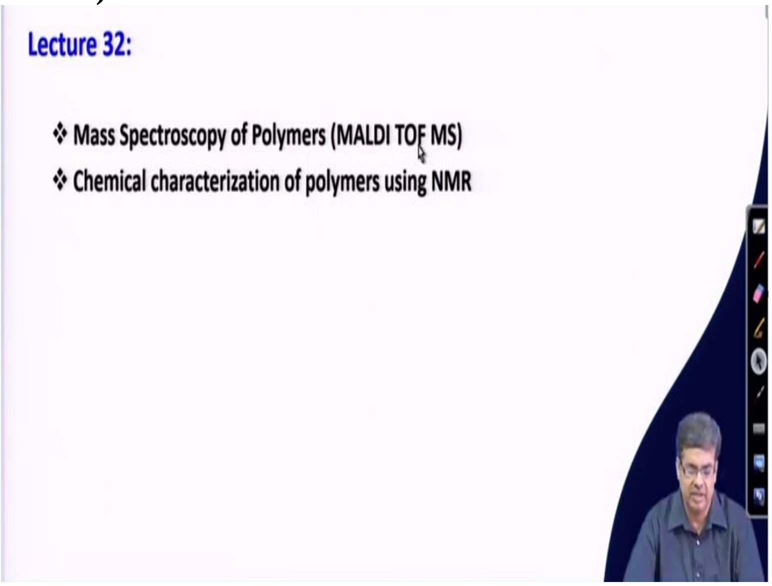

Lecture 32:

- Mass Spectroscopy of Polymers (MALDI TOF MS)
- Chemical characterization of polymers using NMR

So, in this lecture I will talk about mass spectroscopy of polymers, specifically MALDI TOF MS and chemical characterization, restricted to NMR methods.

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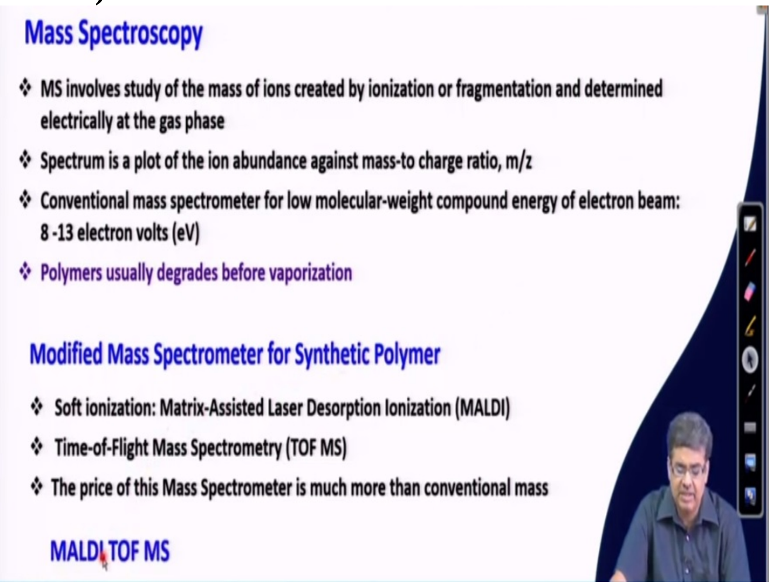

Mass Spectroscopy

- MS involves study of the mass of ions created by ionization or fragmentation and determined electrically at the gas phase
- Spectrum is a plot of the ion abundance against mass-to charge ratio, m/z
- Conventional mass spectrometer for low molecular-weight compound energy of electron beam: 8 -13 electron volts (eV)
- Polymers usually degrades before vaporization

Modified Mass Spectrometer for Synthetic Polymer

- Soft ionization: Matrix-Assisted Laser Desorption Ionization (MALDI)
- Time-of-Flight Mass Spectrometry (TOF MS)
- The price of this Mass Spectrometer is much more than conventional mass

MALDI TOF MS

In general, mass spectroscopy involves study of mass of ions created by ionization or fragmentation, and determine them electrically at the gas phase. Mass spectroscopy spectrum is a plot of ion abundance against mass to charge ratio or in simply m/z. Conventional mass spectrometers are for low molecular compounds, the energy of the electron beam used is about 8 to 13 eV.

In case of polymers if we use this high electron beam to fragment, polymer might degrade before vaporization that will complicate the situation. Further in case of small molecules, small organic molecules, we know that all the molecules have same molecular weight. So, if we fragment, the largest fragment will be of course, coming from the molecular weight itself, the entire whole molecule itself. But in case of a polymer, the sample anyway consists of many molecular weight polymer chains. So, if you fragment a particular polymer, then we do not know whether that fragments are because of fragmentation of a polymer chain or those were present originally in the polymer mixture. So, use of mass spectroscopy in polymer needs to be done in such a way that the polymer chains should not be get fragmented during the measurement. We should be able to measure the molecular ion of all the polymer chains so that we can get the size distribution of the entire mixture of polymer molecules.

For that, modified mass spectrometers are used for synthetic polymers. In this case, soft ionization is done and that is done using a matrix. So, we call Matrix-Assisted Laser Desorption Ionization. I will discuss this process in little detail. The time between detector and the origin is actually measured. That is why we call time of flight, TOF, and the price of this type of mass spectrometers is much higher compared to the conventional mass spectrometer, which are used for determining the molecular weight of small organic molecules. So, in short we call this as MALDI TOF MS.

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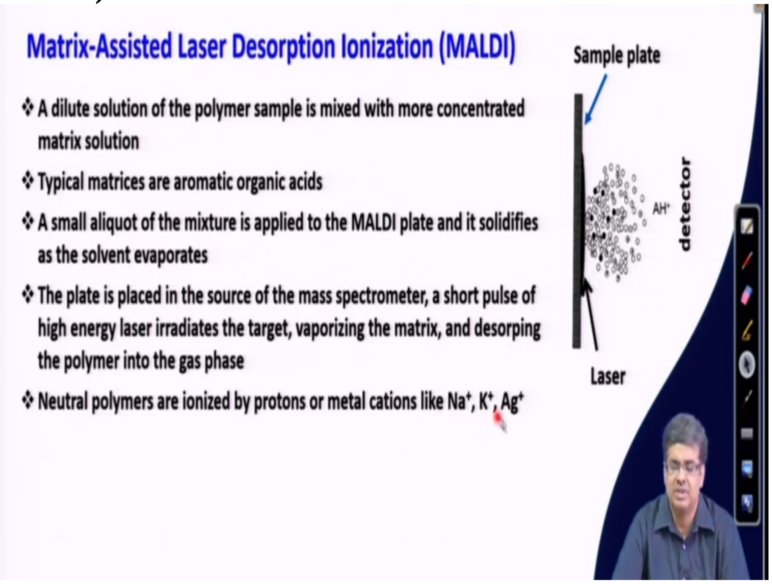

Matrix-Assisted Laser Desorption Ionization (MALDI)

- A dilute solution of the polymer sample is mixed with more concentrated matrix solution
- Typical matrices are aromatic organic acids
- A small aliquot of the mixture is applied to the MALDI plate and it solidifies as the solvent evaporates
- The plate is placed in the source of the mass spectrometer, a short pulse of high energy laser irradiates the target, vaporizing the matrix, and desorping the polymer into the gas phase
- Neutral polymers are ionized by protons or metal cations like Na$^+$, K$^+$, Ag$^+$

Now, as I discussed that, in this case, we cannot fragment the polymer chains. So, soft ionization is required. For that dilute solution of a polymer sample is mixed with a more concentrated matrix solution, the typical matrices are organic, aromatic organic acids. Small aliquot of this mixture is applied to the MALDI plate where it solidifies as the solvent evaporates. Once solvent is evaporated we have the mixture of polymers sample and the matrix.

Now, the plate is placed in the source of mass spectrometer and short pulse of high energy laser irradiates the target. That means, on irradiation this mixture, it actually vaporizes the matrix. Now, once the matrix vaporizes it carries the polymer, which was immersed in this matrix. So, it takes the polymer in vapor phase and in the vapor phase the matrix gets de-sorbed from the polymer molecules. So, we have the polymer molecules in a vapor phase. Polymer molecules need to be charged so that they can move under electric field. Hence, neutral polymers are ionized by protons or small cations like sodium, potassium or silver ion.

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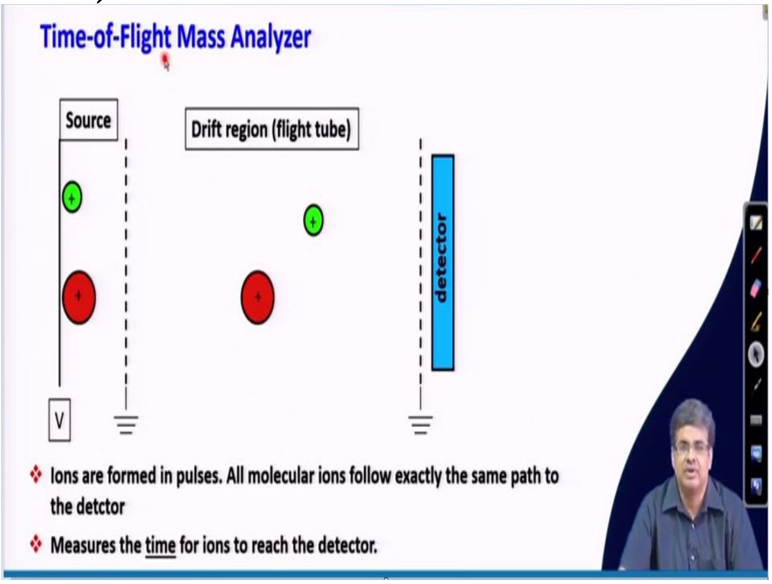

Time-of-Flight Mass Analyzer

- Ions are formed in pulses. All molecular ions follow exactly the same path to the detctor
- Measures the time for ions to reach the detector.

So, once we generate these charged molecular ions, then we apply a detector and the time it takes to move from the source to the detector is what is determined and we call this as time of flight. Obviously, the time will be taken more by the larger molecular weight than the smaller molecular weight. Ions are formed in pulses and all the molecular ions follow exactly the same path to the detectors and the detector measures the time for the ions to reach the detector, this is why the term time of flight is used for this technique.

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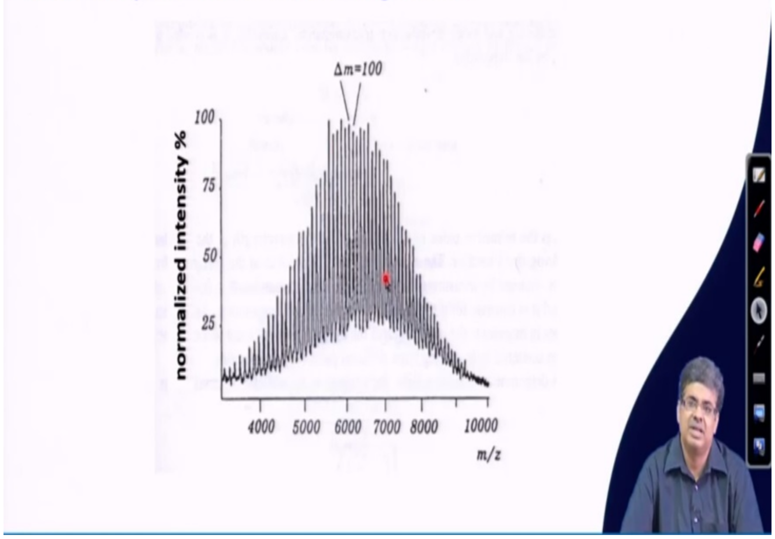

MALDI mass spectrum of low-molecular-weight PMMA

So, this is a typical MALDI spectrum for low molecular-weight PMMA. This technique is mostly useful for low molecular samples because, if the molecules are very large, a high molecular sample, then finding a proper matrix to carry them to the vapor phase is difficult. Hence, it is mostly useful for low molecular sample, but it does not mean that it cannot be used for high molecular weight. Using proper matrix and trial and error method, it is possible to use this technique for high molecular weight as well.

This is an example of MALDI mass spectrum for low molecular-weight PMMA and in this case, you can see that difference between two molecular ions is 100 which is the molecular weight of the repeat unit of PMMA. Thus, it is confirmed that this spectrum is from PMMA and from this distribution we can get the values for M_n and M_w and so on.

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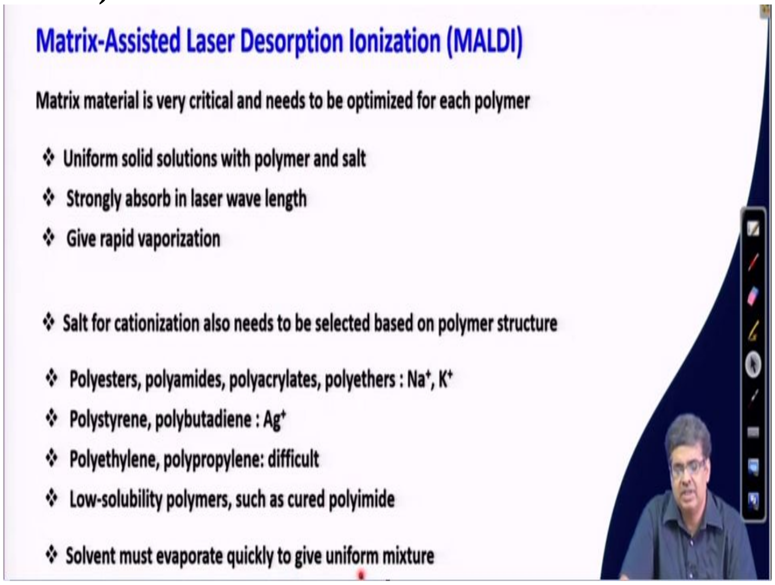

Matrix-Assisted Laser Desorption Ionization (MALDI)

Matrix material is very critical and needs to be optimized for each polymer

- ❖ Uniform solid solutions with polymer and salt
- ❖ Strongly absorb in laser wave length
- ❖ Give rapid vaporization

- ❖ Salt for cationization also needs to be selected based on polymer structure

- ❖ Polyesters, polyamides, polyacrylates, polyethers : Na$^+$, K$^+$
- ❖ Polystyrene, polybutadiene : Ag$^+$
- ❖ Polyethylene, polypropylene: difficult
- ❖ Low-solubility polymers, such as cured polyimide

- ❖ Solvent must evaporate quickly to give uniform mixture

So, matrix material is very critical in this technique and needs to be optimized for each polymer. That is the disadvantage, there is no general rule, there are some guidelines or some kind of guidelines from prior experience about the choice of matrix, but there is no hard and fast rule that a particular matrix would be used for a particular polymer and so on. Uniform solid solution with the polymer and the salt has to be there. The matrix has to strongly absorb the laser in that particular wavelength and it also should give rapid vaporization.

The salt for cationization also needs to be selected based on polymer structure. Generally, for polyester, polyamides, polyacrylates, sodium and potassium ions are used. For more hydrophobic polystyrene, polybutadiene, silver ions are used. Polyethylene and polypropylene are very difficult to ionize using these techniques. So, this technique is not very useful for determining the molecular weight of polyethylene, polypropylene, and in some cases the solubility of the polymers is not good in solvents which need to be used for making a mixture with the matrix which is difficult. So this technique is not useful for those polymers and the solvent must evaporate quickly to give a uniform mixture. These are typical examples of the matrix which are used for this technique.

Next, I will move to the chemical analysis of polymer using NMR. There are other spectroscopic techniques like UV-visible and infrared spectroscopy, which can be used to do chemical analysis.

But, the use of NMR is much more practical and much more useful because use of IR and UV visible spectrum is very limited, these are limited to determination of the functional groups or chromophores present in the polymer molecule itself.

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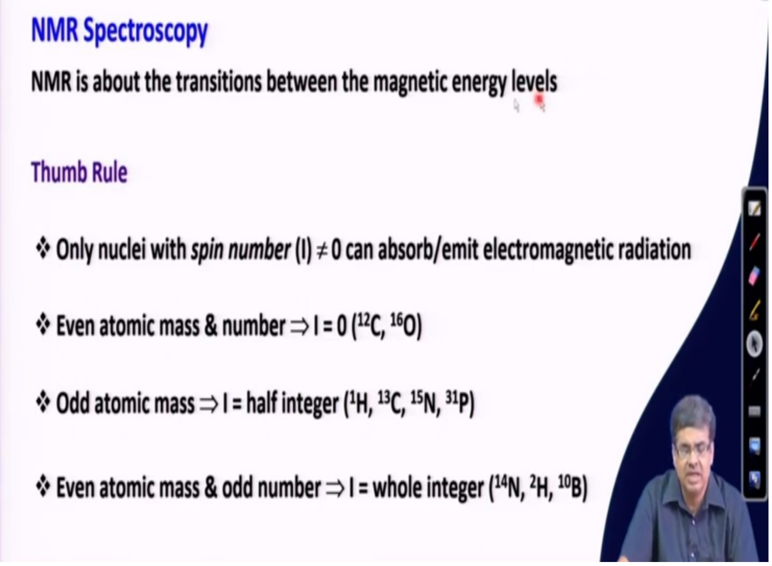

NMR Spectroscopy

NMR is about the transitions between the magnetic energy levels

Thumb Rule

- Only nuclei with *spin number* (I) ≠ 0 can absorb/emit electromagnetic radiation
- Even atomic mass & number ⇒ I = 0 (^{12}C, ^{16}O)
- Odd atomic mass ⇒ I = half integer (^{1}H, ^{13}C, ^{15}N, ^{31}P)
- Even atomic mass & odd number ⇒ I = whole integer (^{14}N, ^{2}H, ^{10}B)

Now, those of you do not know NMR spectroscopy, this is just a quick basic guideline that NMR is about the transitions between magnetic energy levels of a molecule. The thumb rule, about the type of molecules that are NMR active, is that only nuclei with non-zero spin number, $I \neq 0$, can absorb and emit electromagnetic radiation. Atoms, which have even atomic mass and number, are not NMR active because their $I = 0$ like ^{12}C, and ^{16}O which are the most abundant atoms in carbon and oxygen, respectively. Whereas, odd atomic mass gives I = half integers, which are useful for NMR spectroscopy like proton, ^{13}C, ^{15}N, ^{31}P. Atoms with even atomic mass and odd atomic number gives a whole integer like ^{14}N. This can also be used for your NMR spectroscopy.

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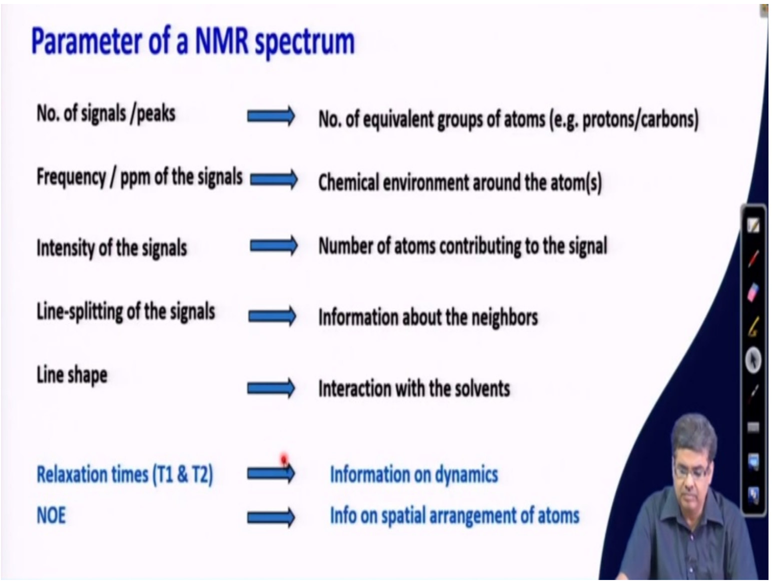

Parameter of a NMR spectrum

No. of signals /peaks → No. of equivalent groups of atoms (e.g. protons/carbons)

Frequency / ppm of the signals → Chemical environment around the atom(s)

Intensity of the signals → Number of atoms contributing to the signal

Line-splitting of the signals → Information about the neighbors

Line shape → Interaction with the solvents

Relaxation times (T1 & T2) → Information on dynamics

NOE → Info on spatial arrangement of atoms

These are the parameters which we obtain from an NMR spectrum. This is a simple guideline for those who are not very habituated with NMR spectrum. The number of signals or peaks in a spectrum is related to number of equivalent group of atoms. For example, number of equivalent protons or ^{13}C present in that molecule. The frequency or the ppm of a signal or the position of a signal is related to the chemical environment around that atom. The intensity of the signal is related to the number of atoms that are contributing to the signal. Line splitting of the signal gives information about the neighbor; the peak line shape provides information about the interaction with solvent. There are some specific specialized techniques, which are not very common. Relaxation time T1, T2 gives the information about polymer dynamics and NOE, which gives you the information about the spatial arrangement of atoms which helps us to find out that polymer confirmation and so on.

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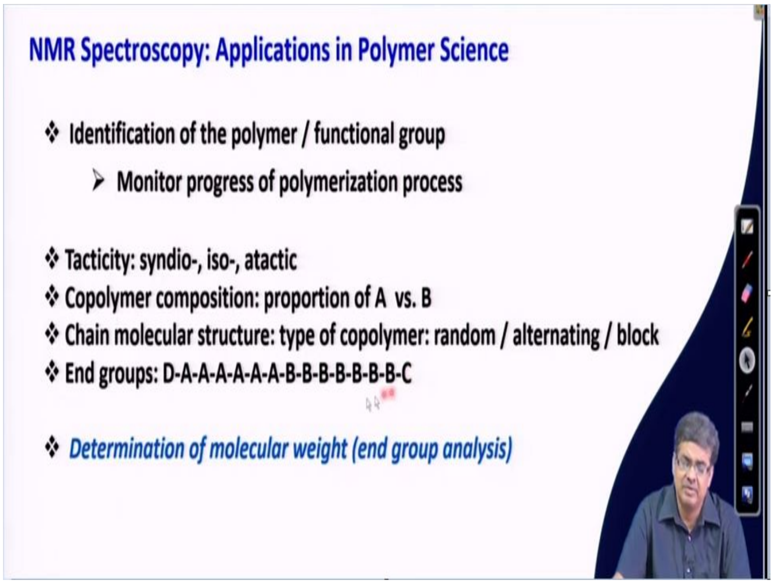

NMR Spectroscopy: Applications in Polymer Science

- Identification of the polymer / functional group
  - Monitor progress of polymerization process
- Tacticity: syndio-, iso-, atactic
- Copolymer composition: proportion of A vs. B
- Chain molecular structure: type of copolymer: random / alternating / block
- End groups: D-A-A-A-A-A-A-B-B-B-B-B-B-B-C
- *Determination of molecular weight (end group analysis)*

NMR spectroscopy is actually used in great detail to identify the polymers and the functional groups, which can be used to monitor the progress of polymerization process. It can be used to find out the tacticity, whether syndiotactic, isotactic or atactic polymer. It can be used for determining copolymer composition, chain molecular structure in a copolymer - random, alternating and block. It can also be used to find out and quantify the end groups. By quantifying end groups, as we mentioned in earlier lecture, NMR can determine the M_n, number average molecular weight as well.

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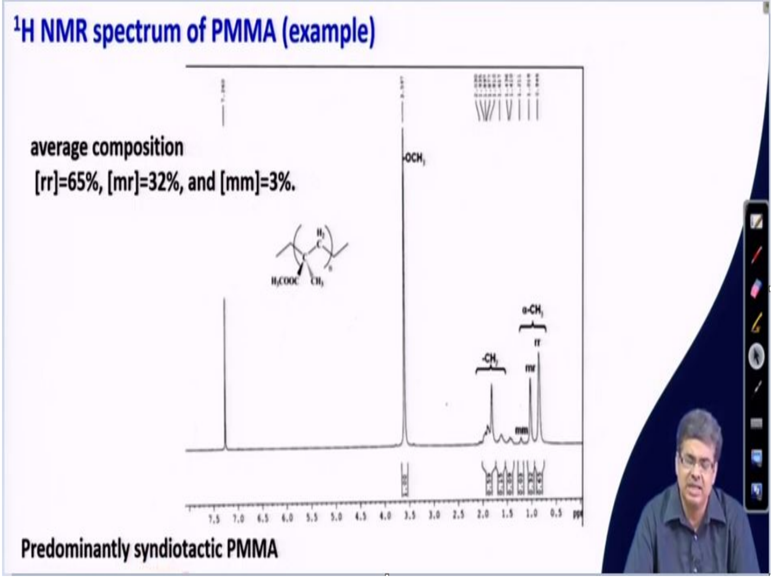

^1H NMR spectrum of PMMA (example)

average composition
[rr]=65%, [mr]=32%, and [mm]=3%.

Predominantly syndiotactic PMMA

This is an example of proton NMR spectrum of PMMA. There are 3 types of protons present in this molecule, 1 here, 2 protons and this is 3 protons and again 3 protons. So, it will have 3 different peaks. So, this peak is here, this is here all 3 and this is here. Now, this methyl can have different stereo arrangement relative to the next repeat unit. Remember we talked about different possibilities - syndiotactic, where the stereo arrangements are alternate, isotactic, when the stereo arrangements are same, and atactic, where there is no particular order of stereo arrangement. Now, in a particular sample, it may not be the case that we have exclusive arrangement of syndiotacticity or atacticity or isotacticity. By comparing this intensity of this signal, which corresponds to one particular arrangement like *rr* corresponds to syndiotactic, *mm* corresponds to isotacticity, this corresponds to atacticity. From the relative intensities, we can actually find out what is the extent of tacticity. For example, in this particular sample, the contribution of *rr* is much higher, which means that this particular sample is predominantly syndiotactic in nature.

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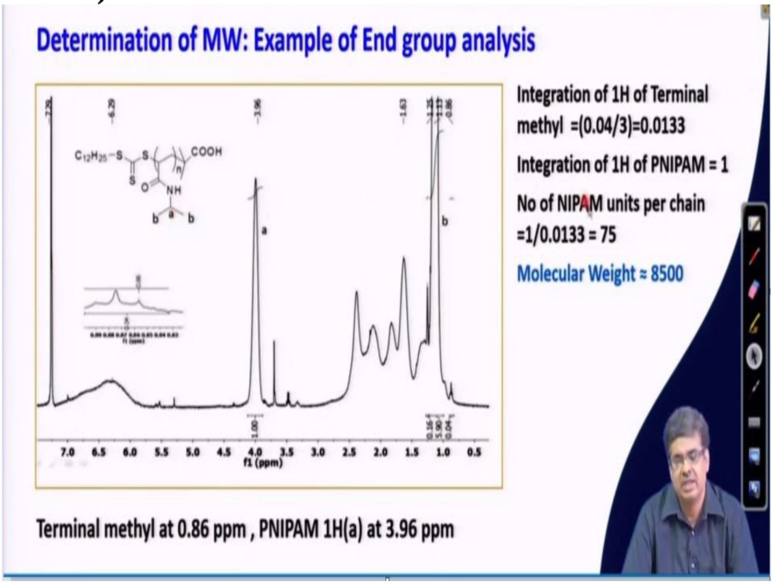

Determination of MW: Example of End group analysis

Integration of 1H of Terminal methyl =(0.04/3)=0.0133

Integration of 1H of PNIPAM = 1

No of NIPAM units per chain =1/0.0133 = 75

Molecular Weight ≈ 8500

Terminal methyl at 0.86 ppm , PNIPAM 1H(a) at 3.96 ppm

Now, I have discussed this earlier also, how to use end group analysis using NMR to determine molecular weight. So, I will not go through this in detail. Just recall that in this particular polymer, as I explained earlier, the molecular weight was found to be 8500 and number of this N-isopropyl acrylamide unit or the value of n was found to be around 75. And this was done by comparing the signal of this particular proton. Here *a* proton which is exclusive to this monomer, and these protons are present in the end group. By comparing these intensities of these two types of protons we can get the value of n and hence, the molecular weight which I discussed earlier.

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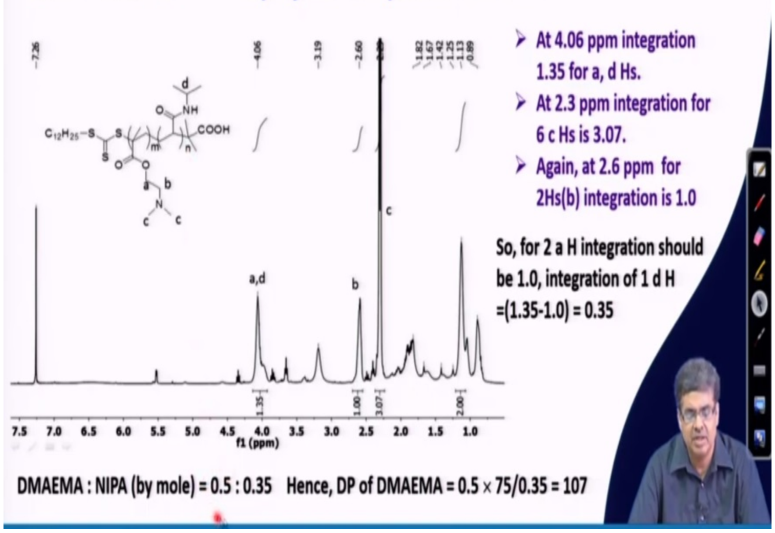

Determination of MW: Copolymer Composition and MW

- At 4.06 ppm integration 1.35 for a, d Hs.
- At 2.3 ppm integration for 6 c Hs is 3.07.
- Again, at 2.6 ppm for 2Hs(b) integration is 1.0

So, for 2 a H integration should be 1.0, integration of 1 d H =(1.35-1.0) = 0.35

DMAEMA : NIPA (by mole) = 0.5 : 0.35 Hence, DP of DMAEMA = 0.5 × 75/0.35 = 107

Now, we can use similar technique to find out the copolymer composition. In this case we have added a second block, dimethyl amino ethyl methacrylate. So, this is the second monomer which we added after the first block was synthesized to make a block copolymer. So, this is a block copolymer of dimethylaminoethyl methacrylate, in short DMAEMA and N-isopropyl acrylamide as we discussed here.

Now, this *d* proton has signal at around 4.06. It has contribution from these protons as well as these protons, 2 protons from this unit and 1 proton from this unit. Whereas, this peak at 2.3 corresponds to these 6 methyl protons and this peak at 2.6 corresponds to these 2 *b* protons. Now, you can also see that these 6 protons give you intensity around 3, whereas, 2 protons give you an intensity around 1, which satisfy the internal calibration. Though it is not perfect, but it is nearly same.

In this combined signal which has contributions from both this monomers, this *d* proton as well as *a* proton, we can use this signal to find out the contribution of this block. In this case, the intensity value is 1.35**.** Now, per proton we should get 0.5 as a signal. So, the 2 protons here we should get a signal corresponds to 1. So, this extra 0.35 must be coming from this proton. So, 0.35 contributions from these protons and 1 from this proton. Hence, the ratio by mole or by number between these two repeat units or ratio of m and n must be 0.5 : 0.35 or the degree of polymerization of this particular unit would be 0.5× 75/0.35 because 75 is the value of n which we have determined in last slide. Hence, the number of units of this particular unit is about 107 or the value of m is 107. This is the example how NMR can be used to determine the composition. Now, this is for block copolymer we can use the same technique to find out the composition in case of random copolymer or other types of copolymers provided we have exclusive peaks for different monomers.

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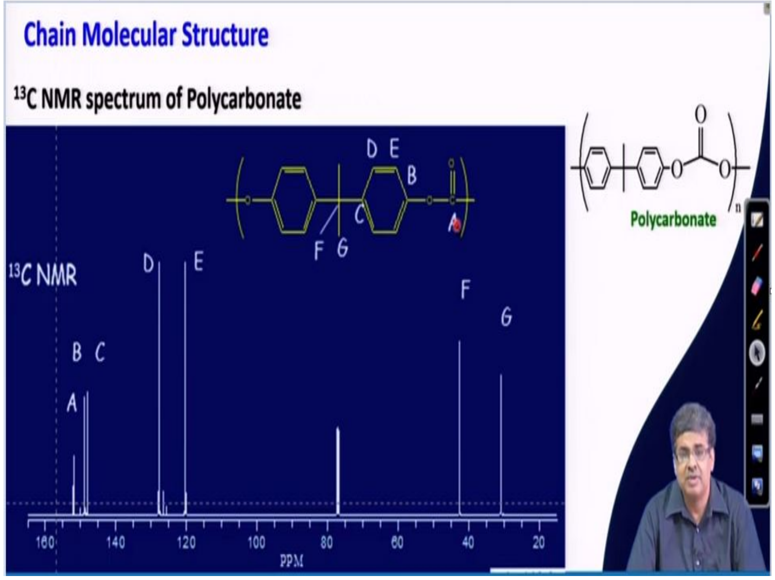

Chain Molecular Structure

^{13}C NMR spectrum of Polycarbonate

We can use ^{13}C NMR to find out the type of copolymer. For example, this is a ^{13}C NMR for polycarbonate, Bisphenol A polycarbonate and each of these carbons are marked here. The carbon peak which is interesting to find out the type of copolymer is *A* which is shown here which will be utilized to find out what is the nature of copolymer.

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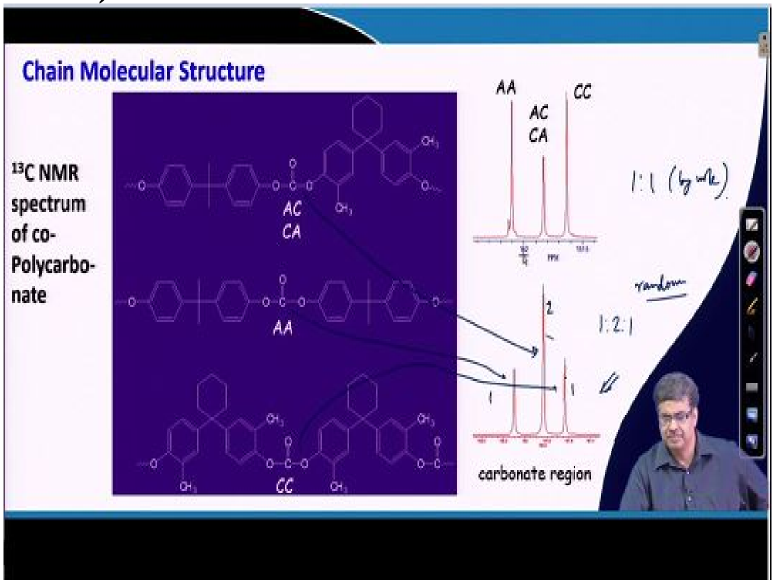

Chain Molecular Structure

^{13}C NMR spectrum of co-Polycarbonate

carbonate region

In this case we have a copolymer of Bisphenol A and this monomer. Now, there are three possibilities in this case. If these two monomeric unit Bisphenol A seat next to each other or they contribute to form this carbonate linkage, then this carbon will have different value than a combination of Bisphenol A and Bisphenol A or this particular monomer with this particular monomer. So, from the value of intensity of this carbon signal we can get what is the arrangement or what is the extent of arrangement of this kind or this kind or this kind in a copolymer. Now, in a statistical sense, if the copolymerization is formed from a 1:1 mixture of these two monomers and if there is no bias between any of these arrangements, then because there are two ways it can be formed, this should have weightage of 0.5, this will 0.25 and this will have 0.25. In this particular case, two monomers are used in 1:1 by mole, and here in this sample, in this carbon has intensity value = 2, this is 1 and this is 1, which means, the ratio of intensity is 2 cases is 1:2:1, which means, in this particular sample, this is a perfect random copolymer of, these 2 monomers. Whereas, in this case you can see that the signal of this particular carbon is lower compared to either of this or this. Hence, we can conclude that the chances or probability of block formation that means, 1 particular monomer is sitting next to same monomer is much high. We can actually compare quantitatively by finding out the ratio of these signal intensities. So, this is not a random copolymer. By using this NMR technique, we can find out whether that 2 monomer actually produces a random copolymer or a non-random blocky type copolymer.

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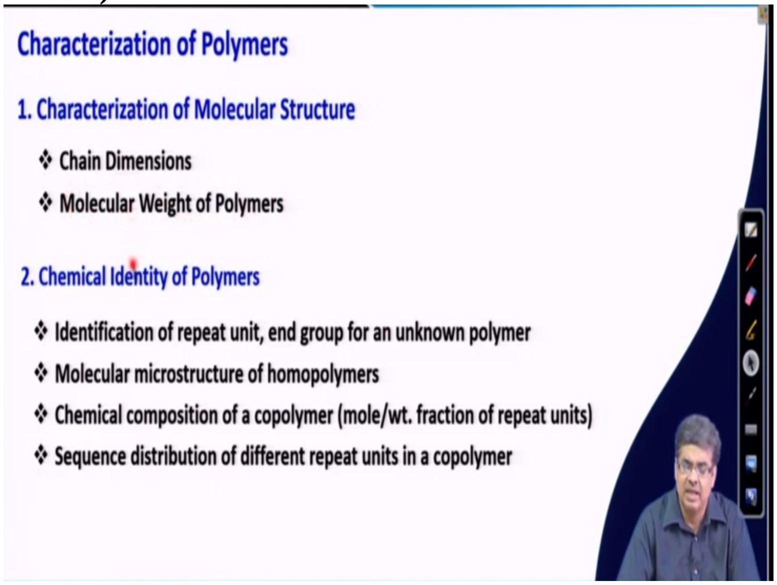

Characterization of Polymers

1. Characterization of Molecular Structure

- Chain Dimensions
- Molecular Weight of Polymers

2. Chemical Identity of Polymers

- Identification of repeat unit, end group for an unknown polymer
- Molecular microstructure of homopolymers
- Chemical composition of a copolymer (mole/wt. fraction of repeat units)
- Sequence distribution of different repeat units in a copolymer

So, with this we have kind of completed the characterization module and if you remember that two main types of calculations we have done. One is molecular structure where we determined the chain dimension and molecular weight of the polymers. And we have found out the identity of the polymers mainly using NMR techniques. I have not gone through the other techniques, which can be used to find out the microstructure involved. There is possibility that we can use the other techniques to find out the microstructure. With this I will conclude this lecture and in next lecture I will start a different module on polymer properties.